

Hydrogen bonded rings are a common structural feature of many host lattices. A reorientational process has been reported in the six-membered ring of O-H...O hydrogen bonds in the clathrate of Dianin's compound (DC) with ethanol [1]. Hydroxyl groups were found to exhibit concerted rotational jumps involving approximate rotations around C-O bonds, thus changing the direction of hydrogen bonding in the ring. Although an analogous six-membered hydrogen bonded ring is present in host structure of hydroquinone, a similar reorientational process has not been reported in any of its clathrates.

We have performed molecular dynamics simulations of the ethanol clathrates of DC and the methanol clathrate of hydroquinone. The simulations reproduce the observed reorientational process in the clathrate of DC but not in the clathrate of hydroquinone. We attribute this difference in behaviour to the larger ring size in the clathrate of DC as well as its greater flexibility.

We have also investigated the role of the guest molecules in the reorientational process. In the case of DC, ethanol appears to serve as a mediator, lowering the activation energy of reorientation through hydrogen bonding to oxygen atoms in the ring. The flexibility of the six-membered ring in DC enables hydroxyl groups of the ring to participate in hydrogen bonds with the guest.

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Keywords: host-guest systems, dynamics, simulations

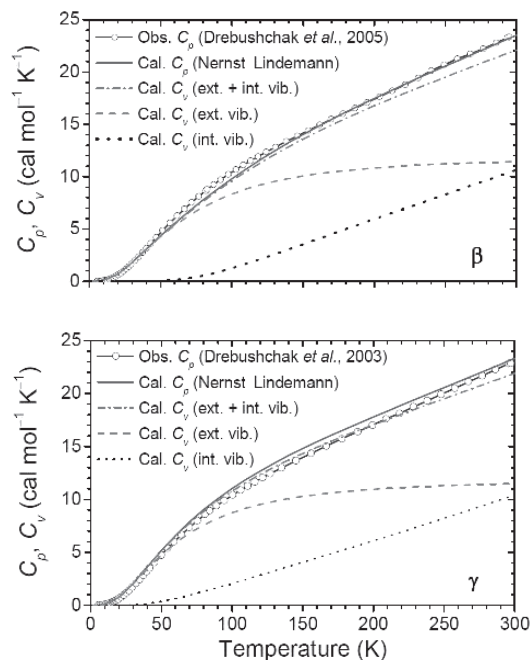
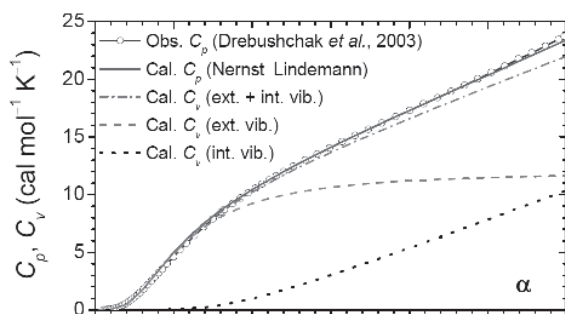
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Dynamic and thermodynamic properties of glycine polymorphs from diffraction data

Thammarat Aree,^a Hans-Beat Bürgi,^b Dmitry Chernyshov,^c Karl W. Törnroos,^d ^aDepartment of Chemistry, Chulalongkorn University, Bangkok, (Thailand). ^bDepartment of Chemistry and Biochemistry, University of Berne, (Switzerland). ^cEuropean Synchrotron Radiation Facility, (France). ^dDepartment of Chemistry, University of Bergen, (Norway). E-mail: thammarat.aee@gmail.com

Synchrotron data to 0.5 Å resolution of the α -, β - and γ -polymorphs of glycine were collected between 10 and 298 K at KEK, SPring-8 and the ESRF. Data were processed with RAPID AUTO, DENZO/SCALEPACK or SAINT+ and structures were refined with SHELXL-97, yielding $R_{\text{int}} \approx R_1 \leq 5\%$. Simultaneous analyses of the multi-temperature atomic displacement parameters were performed to obtain librational and translational frequencies [1]. The external vibration frequencies from a normal mode analysis and the internal vibration frequencies from a two-layer ONIOM(B3LYP/6-311+G(2d,p):PM3) method and a glycine cluster model were used together with the Einstein, Debye, and Nernst-Lindemann molecular models to determine heat capacities C_V , C_p that are in agreement with C_p from calorimetry [2-3].



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Keywords: dynamics, thermodynamics, polymorphs

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Observation of the photo-excited state of $[\text{Co}^{\text{III}}(\text{en})_3]^{3+}$ by picosecond time-resolved XAFS

Tokushi Sato,^a Shunsuke Nozawa,^a Ayana Tomita,^a Manabu Hoshino,^{b,c} Shin-ya Koshihara,^{b,c} Munetaka Iwamura,^d Shin-ichi Adachi,^{a,e} ^aPhoton Factory (PF), High Energy Accelerator Research Organization, Ibaraki, (Japan). ^bDepartment of Chemistry and Materials Science Tokyo Institute of Technology, Tokyo, (Japan). ^cCREST, (Japan) Science and Technology Agency (JST). ^dGraduate School of Science and Engineering, University of Toyama, Toyama, (Japan). ^ePRESTO, (Japan) Science and Technology Agency (JST). E-mail: tokushi.sato@kek.jp

Studying photochemical reaction in liquid with subnanosecond time-resolution gives information for understanding fundamental chemistry, biology and also for developing new materials and devices. [1]-[4] Monitoring the dynamic phenomenon requires a sensitive tool to investigate the electronic state and the structure with atomic resolution. However, studies of the excited state of tris(ethylenediamine)cobalt(III) ($[\text{Co}^{\text{III}}(\text{en})_3]^{3+}$) have been performed only using optical spectroscopic methods, [5] from which it is difficult to estimate the molecular structure with atomic resolution. Here, we have performed time-resolved X-ray absorption fine structure (TR-XAFS) on the $[\text{Co}^{\text{III}}(\text{en})_3]^{3+}$ dissolved in aqueous.

All measurements were performed in fluorescence method at the cobalt K-edge on the undulator beamline NW14A at the Photon Factory Advanced Ring. [6] X-ray pulses at 794 kHz were monochromatized by a Si(111) monochromator and used for the probe. A third harmonic of Ti:Sapphire laser operating at a frequency of 945 Hz was used for the pump source. The pump and probe measurements were performed

by detecting the fluorescence X-ray signals just after and just before the laser pulse using gated integrators synchronized with the laser pulse (945 Hz). [7] Obtained results clearly demonstrate the success in probing both structural and electronic state changes induced by 267nm femtosecond laser pulse excitation with 100ps resolution.

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Keywords: XAFS, dynamics, photochemistry

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Development for X-ray Crystal Structure Analysis of a Surface-Shallow Layer

Koshiro Toriumi,^a Hiroaki Yamanaka,^a Aki Takazaki,^a Daisuke Yamashita,^a Minoru Mitsumi,^a Yoshiki Ozawa,^a Osamu Sakata,^b
^a*Department of Material Science, University of Hyogo, Kamigori-cho, Hyogo (Japan).* ^b*National Institute for Materials Science/SPring-8, Sayo-gun, Hyogo (Japan).* E-mail: toriumi@sci.u-hyogo.ac.jp

Chemical and physical phenomena that happen in a shallow layer of a crystalline material such as photo-induced chemical reaction and transport of small molecules on crystal surface should be elucidated more clearly if three-dimensional structure of the crystal surface layer up to 1 μm in depth could be determined by a depth-resolved X-ray diffraction technique. This new diffraction method could be achieved by measuring diffraction intensities on the condition of exactly controlling the X-ray penetration depth.

Epitaxial crystals of the halogen-bridged mixed-valence platinum(II,IV) complexes should be suitable to evaluate whether the structure analysis of a surface shallow layer can be achieved. The surface film crystal of the chloro-bridged platinum(II,IV) complex (1) was successfully crystallized on the (001) plane of the bromo-bridged platinum(II,IV) base crystals (2) which was isomorphous to (1) with slightly different cell dimensions. The X-ray diffraction experiments were performed using the multi-axis diffractometer at SPring-8 BL13XU. The epitaxial crystals of (1) that grows up on the substrate of (2) with dimensions of 1.25x0.5 mm by thickness of about 0.3 μm was investigated.

Out-of-plane reflections were measured using 8 keV X-ray beam focused on 3x4 μm with 2D lens for a grazing incident angle of 0.1°–0.7°. The diffraction image measured for a grazing incidence of 0.3° is shown in Figure 1. Reflections from the surface film crystal of (1) and those from the substrate of (2) are observed as sharp Bragg spots without powder lines. The reflection pairs with the same indexes are located at neighboring positions. This indicates that the epitaxial film crystal is just a single crystal with its orientation being almost the same as the substrate crystal. Integrated intensities of both the film and substrate crystals were obtained. Although the measured intensity ratios of the film crystal to the substrate become smaller as incident

angle increase, its decreasing ratio is smaller than the value calculated for the thickness of the film crystal. This suggests that it is necessary to improve smoothness on the crystal surface.

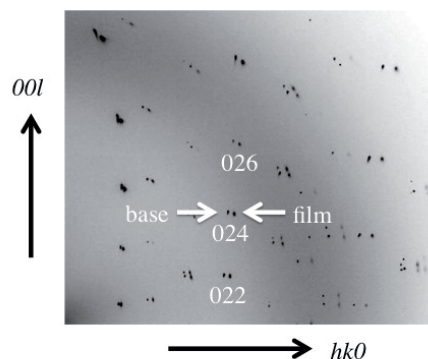


Fig. 1. Diffraction images measured for a grazing angle of 0.3°.

Keywords: surface, structure, epitaxial

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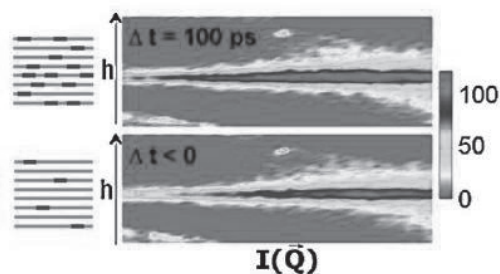
Evidence of one-dimensional precursors in the photoinduced transformation in TTF-CA

Laurent Guérin,^{a,b} Eric Collet,^a Johan Hébert,^a Marylise Buron-Le Cointe,^a Shin-ichi Adachi,^b Shin-ya Koshihara,^b Hervé Cailleau^a
^a*Institut de Physique de Rennes, Université de Rennes1, (France).* ^b*JST Exploratory Research for advanced Technology, Tsukuba, (Japan).* E-mail: laurent.guerin@univ-rennes1.fr

The photoinduced phase transition in TTF-CA was intensively studied the last ten years both experimentally and theoretically [1–4]. It is the archetype organic system where cooperativity [1] and coherence [5] play a major role in the transformation. Here we investigate the precursors of the photoinduced phase transition in the highly cooperative charge-transfer molecular crystal TTF-CA and provide key insights. The photogeneration of one-dimensional nanoscale clusters was detected by time-resolved diffuse x-ray scattering with 50-ps time resolution at NW14 beamline, KEK, Japan.

The mapping of the diffuse plane shows a time dependence after excitation and is the direct signature of the formation of 1D clusters induced by light occurring at the first step of the photoinduced phase transition. [6]

Such clustering of structurally relaxed electronic excitations is expected to be a common process in many materials presenting photoinduced transformations.



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